

CARBONYL SULFIDE: PROGRESS IN RESEARCH AND COMMERCIALIZATION OF A NEW COMMODITY FUMIGANT

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Introduction

The use of carbonyl sulfide (COS) as a fumigant for durable commodities and structures was patented worldwide in 1992 by CSIRO Australia (Banks *et al.* 1992). COS has the potential to replace methyl bromide in several of its applications for durable commodities, and also to be used as an alternative to phosphine when there is a significant problem with insect resistance. This paper summarises research results primarily from the fumigant research group within the Stored Grain Research Laboratory and CSIRO's progress towards commercialisation of this fumigant.

Performance as a fumigant

COS is effective on a wide range of pests, including the common stored product species at reasonable concentrations ($<50\text{gm}^{-3}$) and exposure times (1-5 days) (Desmarchelier 1994, Zettler *et al.* 1997). Of these, *Sitophilus oryzae* is the most naturally tolerant and in-depth studies have been conducted on this species. These studies provide a range of exposure time/concentration regimes to give disinfestation level mortalities. They show concentrations of 20 gm^{-3} for an exposure time of 5 days to be a particularly good combination although there are other possible combinations (Weller 1999).

Sorption studies have been carried out in the laboratory on wheat, oats, barley, paddy rice, sorghum, mung beans, canola, peanuts, sultanas, and hard and soft timbers. All these materials have sorption rates and levels compatible with COS as a fumigant. Sorption studies with excessively wet commodities, such as wheat at $\geq 18\%$ moisture content, show a rapid loss of COS at rates that would make COS fumigation impracticable.

A series of field trials on wheat (Desmarchelier *et al.* 1998), oats, barley and canola (Ren *et al.* in press) have been conducted 50 tonne silo bins. These trials were undertaken to start the formal path towards registration, to validate laboratory predictions in the field, to demonstrate compliance with OH&S standards, to produce industry sized parcels of grain to allow industry assessment of quality, and to assess the time required for venting and clearing larger bulks of grain. All these goals were met and the trials so far have not shown any actual or potential problems in the large-scale use of COS. On the other hand, they have shown that safe and effective fumigation should be possible within the competency of a skilled fumigator. Larger scale trials of ≥ 700 tonnes of commodity will be undertaken in the next year, primarily to optimize application methods.

Post fumigation residues of COS in the above trials were found to be below the provisional Australian experimental MRL of 0.2 mg kg^{-1} after 4 hours of airing. Therefore, the field trials confirmed that COS can be completely 'aired-off' from the commodity after fumigation and thereafter, that COS levels in fumigated grains and seeds are indistinguishable from the levels in untreated commodities. This is both due to the fast desorption of COS from commodities after fumigation and to the very low, but natural, presence of COS in grains and seeds (around $0.05 - 0.1 \text{ mg kg}^{-1}$).

COS has minimal effect on treated durable commodities. Detailed quality tests from the field trials showed no adverse effect on quality of bread, noodles or sponge cake (wheat) (Desmarchelier *et al.* 1998), on malt or beer (malting barley) or on oil content or oil color (canola) (Ren *et al.* 2000). Germination of seed (wheat, oats, barley, canola) was also unaffected by fumigation by COS.

Reaction with other materials

A number of materials were exposed to high concentrations of COS (at high temperature and r.h.) without obvious effect on the material or on the concentration of COS remaining in, or available to, the gas space. The materials were hard and soft timbers, paper, iron, steel and galvanised sheet, PVC, polyethylene, and brick. Loss of COS on fresh concrete was rapid, but loss on aged concrete was minimal.

Interactions between COS and copper have been the object of several laboratory investigations both in Australia and in Germany (Ren *et al.* in press). These have found that pure COS or COS with $<0.1\%$ H_2S does not corrode copper, but COS significantly contaminated with H_2S does. This indicates that the COS used for commercial fumigations must be substantially free of H_2S .

Toxicology and Environmental Aspects

Fumigants employed for grain protection must undergo toxicological testing to provide a basis for the protection of workers that may be exposed to the chemical and for consumers of the treated commodity. COS has not been registered previously for use as an agricultural chemical. Although the toxicological database for COS is small, published studies do not indicate any concerns regarding the success of COS in a toxicity testing battery. The toxic metabolite of COS, hydrogen sulfide (H_2S), has a well-characterised toxicity spectrum.

COS is the major sulfur chemical naturally present in the atmosphere at $0.5 (\pm 0.05) \text{ ppb}$ and is an important part of the global sulfur cycle (Ren 1999). That is, humans are continually exposed to low concentrations of this chemical. In addition, other low-level human exposures to COS arise from its presence in foodstuffs such as cheese and prepared vegetables of the cabbage family. COS is naturally present in grains and seeds in the range of $0.05\text{-}0.1 \text{ mg kg}^{-1}$.

Commercialization

CSIRO is currently in discussion with a number of selected companies and consortia that have the capacity to manufacture, distribute and market COS worldwide.

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